

E900759

NWC TP 6839

(4)

DTIC FILE COPY

Electrochemical Studies of the TIN(IV)-Pyrocatechol Violet System

by
Dwight A. Fine
Research Department

OCTOBER 1987

DTIC
ELECTE
JAN 12 1988
S D

NAVAL WEAPONS CENTER
CHINA LAKE, CA 93555-6001



Approved for public release;
distribution is unlimited.

AD-A197 451

88 1 5 007

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

AD-A197451

REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION UNCLASSIFIED			1b RESTRICTIVE MARKINGS	
2a SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Public release; distribution unlimited.	
2b DECLASSIFICATION/DOWNGRADING SCHEDULE				
4. PERFORMING ORGANIZATION REPORT NUMBER(S) NWC TP 6839			5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a NAME OF PERFORMING ORGANIZATION Naval Weapons Center		6b OFFICE SYMBOL (If applicable)		7a NAME OF MONITORING ORGANIZATION
6c ADDRESS (City, State, and ZIP Code) China Lake, CA 93555-6001			7b ADDRESS (City, State, and ZIP Code)	
8a NAME OF FUNDING/SPONSORING ORGANIZATION		8b OFFICE SYMBOL (If applicable)		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c ADDRESS (City, State, and ZIP Code)			10. SOURCE OF FUNDING NUMBERS	
			PROGRAM ELEMENT NO. 61152N	PROJECT NO. ZR00001
			TASK NO. ZR000010	WORK UNIT ACCESSION NO. 13805018
11 TITLE (Include Security Classification) ELECTROCHEMICAL STUDIES OF THE TIN(IV)-PYROCATECHOL VIOLET SYSTEM				
12 PERSONAL AUTHOR(S) Fine, Dwight A.				
13a TYPE OF REPORT Final		13b TIME COVERED FROM 86 Jan TO 87 Apr		14 DATE OF REPORT (Year, Month, Day) 1987, October
15 PAGE COUNT 22				
16 SUPPLEMENTARY NOTATION				
17. COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP		
			Analysis, Electrochemistry, Voltammetry, Chromatography, Tin, Organotin, Toxic, Water	
19 ABSTRACT (Continue on reverse if necessary and identify by block number)				
<p>(U) In an effort to develop simpler methods for the analysis of natural waters for toxic organotin compounds, we have studied the electrochemical properties of pyrocatechol violet (PCV) and the complex formed by this reagent with tin(IV) (Sn(IV)). The reagent and the complex were found to show oxidative response to a glassy carbon electrode. Concentrations of tin as low as 200 parts per billion were detectable by oxidative linear sweep voltammetry. Because of the decrease in the height of a characteristic PCV peak upon addition of Sn(IV), formation of the complex was also detectable by liquid chromatography with electrochemical detection. Neither method proved responsive to organotin, although response was observed upon conversion of organotin to inorganic Sn(IV).</p>				
20 DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21 ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED	
22a NAME OF RESPONSIBLE INDIVIDUAL Dwight A. Fine			22b TELEPHONE (Include Area Code) 619-939-1638	22c OFFICE SYMBOL 3851

DD FORM 1473, 84 MAR

83 APR edition may be used until exhausted.
All other editions are obsolete

SECURITY CLASSIFICATION OF THIS PAGE

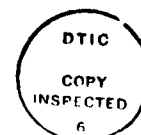
U.S. Government Printing Office: 1985-507-647

UNCLASSIFIED

CONTENTS

Introduction	3
Apparatus and Materials	4
Voltammetric Studies	5
LCEC Studies	7
Summary	8
References	9
Figures	11
Tables	19

Accession For	
NTIS CRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution	
Availability Codes	
Dist	Avail and/or Special
A-1	



INTRODUCTION

Organotin compounds have found extensive use as antifoulants in coatings for ship hulls. When organotin moieties are leached into harbor waters, their biocidal activity becomes undesirable. Efforts have been made in the development of coatings that release organotin at rates slow enough to minimize hazards to marine life. Organotin is most often added to coatings in the form of tributyltin(IV) compounds, usually chloride, hydroxide, oxide, or acetate. More recently, copolymers of tributyl tin with methyl methacrylate have been used to achieve slower release rates. The species formed in sea water by leaching are believed to be primarily tributyltin(IV) hydroxide (Bu_3SnOH) or tributyltin(IV) chloride (Bu_3SnCl), where Bu = butyl (References 1 and 2). These compounds can undergo degradation to dibutyl and monobutyl species and to inorganic tin. Inorganic tin also occurs naturally in sea water in trace amounts as hexahydroxytin(IV) ($\text{Sn}(\text{OH})_6^{2-}$) (Reference 3). In order to monitor rates of leaching, some means of analysis of natural waters for organotin is necessary.

The most accurate method that has been developed involves conversion of the organotin compounds to tin hydrides, followed by chromatographic separation of the hydrides and detection by atomic absorption spectroscopy (References 4 through 6). This method involves expensive apparatus and rather complex work-up procedures. Simpler methods, preferably adaptable to on-site monitoring, are a desirable goal.

The work described in this report resulted from attempts to find a simple electrochemical method for analysis of organotin. Organotin compounds have been determined by polarographic methods involving dropping mercury or hanging mercury drop electrodes (References 7 through 9), but the use of a mercury electrode presents disadvantages for on-site instruments due to the storage, cleaning, and toxicity problems associated with mercury.

There are a variety of methods for determination of inorganic tin(IV) ($\text{Sn}(\text{IV})$). Conversion of organotin(IV) compounds to inorganic $\text{Sn}(\text{IV})$, followed by analysis for $\text{Sn}(\text{IV})$, would enable determination of both total tin and the fraction present as organotin. Electrochemically, inorganic $\text{Sn}(\text{IV})$, like organotin(IV), is usually determined by reduction at mercury electrodes. Spectrophotometrically, the most sensitive method for determination of $\text{Sn}(\text{IV})$ involves conversion to a complex with pyrocatechol violet (PCV), followed by measurement of the absorbance of the complex. This method has been employed for analyses of environmental samples (References 10 and 11).

The structure of PCV is shown in Figure 1. We may refer to this structure as H_4L . Studies have shown the optimum pH for spectrophotometric determination to be between 2 and 3; in this region, PCV exists mainly in the form of H_3L^- , which reacts with Sn^{4+} to form $Sn(H_2L)_2$ (Reference 12).



Since the coordinated and uncoordinated ligands contain hydroxyl groups that are electrochemically oxidizable and coordination tends to modify electrochemical behavior of ligands, there is a possibility of determination of the $Sn(IV)$ -PCV complex by oxidative electrochemistry. Because the removal of dissolved oxygen from the solutions being analyzed is not required, oxidative measurements are more convenient than reductive measurements. The use of a solid working electrode, rather than mercury, would be another advantage.

This report summarizes the results of electrochemical investigations of the $Sn(IV)$ -PCV system. During the investigation two techniques were employed: linear sweep voltammetry (LSV) and liquid chromatography with electrochemical detection (LCEC).

APPARATUS AND MATERIALS

Voltammetric measurements were made with a polarographic analyzer (Model 174) from Princeton Applied Research, Princeton, N.J., operated in the direct current mode. The working electrode was a glassy carbon electrode (GCE) and the reference electrode was a standard calomel electrode (SCE), both obtained from IBM Instruments, Danbury, Conn. The auxiliary electrode was a platinum wire. All potentials given in this report are relative to SCE. The cell was a glass cell obtained from IBM Instruments that was fitted with a plastic screw-on cover containing inlets for electrodes, and reagent and inert gas addition.

Liquid chromatographic separation with electrochemical detection was carried out with a LCEC Analyzer from Bioanalytical Systems (BAS), West Lafayette, Ind., consisting of a basic high performance liquid chromatograph (HPLC) system, an LC-4B electrochemical detector, LC-22A temperature controller, and a dual pen recorder. All experiments used a 25 cm Biophase ODS C-18 column and a GCE cell with an SCE reference electrode at 25°C.

Tri-n-butyl tin(IV) chloride (95+%) and PCV were obtained from Alfa Products, Danvers, Mass. Standard $Sn(IV)$ was AA Standard solution in 20% hydrogen chloride (HCl) that contained 1000 microgram (μg) Sn /microliter (mL); this solution was also obtained from Alfa Products.

Solvents for LCEC work were HPLC grade. Salts used in preparing buffer solutions were filtered through 0.20 micrometer (μM) filters, obtained from BAS. Nitrogen was bubbled continuously through the mobile phase reservoir. Samples were filtered through 0.5 μM Millipore filters prior to injection.

VOLTAMMETRIC STUDIES

Solutions of PCV, standard Sn(IV) and tributyltin(IV) chloride were examined by LSV. Initially, 0.1 molar (M) sodium chloride (NaCl) was employed as the neutral electrolyte, and the pH was adjusted with hydrochloric acid or ammonium hydroxide. When scanned oxidatively from 0.0 to +1.0 volt (V) at 20 millivolts/second (mV/s), highly acidic solutions of PCV show a single current maximum, at about +0.45 V . This peak shifts to lower potentials with increasing pH and disappears at pH greater than 8.5. At pH greater than 1.0, a wave appears at about +0.75 V . This wave shifts to lower potentials with increasing pH, and has virtually disappeared at pH 10. Representative voltammograms are shown in Figure 2, and principal features are summarized in Table 1. The voltammograms reflect the dependence of oxidation waves on the degree of protonation of the PCV molecule.

Results for a series at constant pH (2.2) with varying PCV concentration are shown in Figure 3. Response is linear over most of the concentration range (8.4×10^{-6} to 1.0×10^{-4} M) and is best for +0.76 V .

The effect of adding inorganic Sn(IV) to solutions of PCV is shown in Figure 4. Behavior as a function of pH is summarized in Table 2. Studies were confined to acidic pH values in order to minimize hydrolysis of Sn^{4+} . The pH region between 2 and 4 appears to be the optimum region for the effect of Sn(IV) on oxidative LSV behavior of PCV. At the current range employed, a concentration of 0.5 parts per million (ppm) tin gave a detectable response.

Subsequent voltammetric studies were run on solutions buffered to pH 2.3 with 0.04 M chloroacetic acid (HClOAc) and 0.01 M sodium acetate (NaOAc). The buffer salts served as the supporting electrolyte. In order to correspond closely to the conditions employed in the LCEC measurements described on page 7 and to permit solubility of tributyltin(IV), most solutions were prepared in a 30/70 volume/volume (v/v) mixture of methanol (MeOH) and water.

Voltammograms for a series with PCV concentration constant at 5.2×10^{-5} M and Sn(IV) concentration ranging from 1.6×10^{-6} M to 1.3×10^{-5} M are shown in Figure 5. Results for a similar series, using a smaller current range and scanning only the region between +0.56 and +0.90 V , are shown in Figure 6. A concentration of 1.6×10^{-6} gram-atoms/L (0.2 ppm) of tin gives a detectable response.

The optimum concentration of PCV was found to be about 5×10^{-5} M. More concentrated solutions showed lower sensitivity to Sn(IV). Results for one such series are shown in Figure 7. Lower current range settings were needed at lower concentrations; this created problems because of the high background current due to uncomplexed PCV--a high offset was needed to bring the voltammograms onscale.

If the current at a given potential is represented by i_{obs} , the current due to free PCV by i_{PCV} , the current due to the Sn-PCV complex by i_{com} , and the base current by i_b , then

$$i_{obs} = i_{PCV} + i_{com} + i_b \quad (2)$$

If the complexation reaction is given by



where q is the total charge of the n complexed PCV ions, then the concentration of free PCV is given by

$$[PCV] = \Sigma PCV - n[Sn(PCV)_n^{4-q}], \quad (4)$$

where ΣPCV = total PCV concentration. Assuming that essentially all of the tin is complexed, we have

$$[PCV] = \Sigma PCV - n\Sigma Sn, \quad (5)$$

where ΣSn = total tin concentration. If i_{PCV} is proportional to $[PCV]$ and i_{com} is proportional to Sn , then

$$i_{obs} = k_p[PCV] + k_s\Sigma Sn + i_b = k_p[\Sigma PCV - n\Sigma Sn] + k_s\Sigma Sn + i_b. \quad (6)$$

If we represent i_{PCV} before addition of any tin by i_{PCV}^0 , then

$$i_{Sn=0} = i_{PCV}^0 + i_b = k_p \Sigma PCV + i_b, \quad (7)$$

and the change in current due to addition of Sn is

$$i_{obs} - i_{Sn=0} = [K_s - nK_p] \Sigma Sn. \quad (8)$$

Hence plots of $i_{obs} - i_{Sn=0}$ versus ΣSn should be linear, if n is constant. Under the conditions of pH and concentration employed here, n should be close to 2 (Reference 12), and PCV must be kept greater than or equal to 2 ΣSn . Plots for two fixed potentials, using data from Figures 6 and 7, are shown in Figure 8. Such plots were, in general, only approximately linear, with the greatest deviations from linearity occurring at PCV to tin ratios less than 4. In practice, empirical plots of observed current versus tin concentration would be employed as standard curves.

In order to investigate applicability to analysis for organotin, the response of Bu_3SnCl to PCV was studied. For these experiments, a

solution of 3.7×10^{-3} M Bu_3SnCl in methanol was used as a standard solution. Addition of Bu_3SnCl to the electrolyte solutions employed in the measurements described previously produced no oxidative or reductive waves on the GCE. Addition to solutions of PCV produced no color changes and no changes in oxidative scans. Evidently, the butyl groups in Bu_3SnCl are bound much more strongly to tin than are the coordinated ions in the PCV complex. When a sample of Bu_3SnCl was converted to inorganic tin by fuming with sulfuric acid, and the resultant residue was dissolved in water and added to PCV solution, an oxidative wave was seen. Results from one such experiment are shown in Figure 9. Thus, the detection methods described in this report would not respond to very dilute solutions of organotin, but would require preconcentration and conversion to inorganic tin.

Throughout the investigation, problems with reproducibility of voltammograms were encountered. Such problems are common with solid electrodes, partly because of surface phenomena. Second scans of a given solution usually showed a lower response than the first scans. Polishing the GCE with polishing strips seemed to improve response, but results were not consistent. Aging of solutions also affected response. It would probably be advisable to set up a new standard curve each time the method was employed for analysis.

LCEC STUDIES

All mobile phases for LCEC studies were 0.04 M in chloroacetic acid and 0.01 M in sodium acetate. Initial runs were made with mobile phases 30/70 v/v in methanol/water, with the GCE set at +0.700 V and a flow rate of 1.0 mL/minute (min). When solutions of PCV in solvents having the same composition as the mobile phases were injected onto the column, four weak bands with retention times of 3.5, 4.3, 4.8, and 5.3 minutes were observed, plus a much higher, broader band with a retention time of about 21 minutes. Addition of Sn(IV) to the PCV solutions prior to injection produced no consistent effect on the early peaks, but seemed to decrease the height of the late peak.

Tests in variations of the GCE potential showed a response for PCV at potentials greater than or equal to +0.50 V. The response increased with increasing potential, with a leveling-off trend noticeable at greater than +0.70 V. A potential of +0.800 V was selected for the remainder of the LCEC studies.

An increase in the fraction of methanol present in the mobile phase produced a dramatic decrease in retention time of the main peak. An increase in peak height for a given concentration of PCV was also noted. Results for solutions containing 5.2×10^{-4} M PCV (200 ppm) are shown in Table 3.

Addition of standard Sn(IV) to PCV solutions prior to injection consistently produced a decrease in height of the principal peak. No additional peaks were seen. The decrease in peak height appeared to be proportional to tin concentration at molar ratios of PCV to tin greater than or equal to 4. This indicates that only uncomplexed PCV is detected by the LCEC under the conditions employed. The decrease in peak height is caused by partial complexation of the PCV by Sn(IV). Representative chromatograms for two experiments are shown in Figures 10 and 11. At PCV concentrations below 50 ppm, interference from peaks near the solvent front became a problem.

Data from a series of solutions containing 100 ppm PCV and 2 to 10 ppm Sn(IV) are shown in Figure 12. Figure 13 is a plot of average decrease in peak height versus Sn(IV) concentration. The decrease is linear up to 8 ppm Sn(IV), which corresponds to molar ratios of PCV to tin greater than or equal to 3.8. The slope of the linear portion corresponds to 5.6 nanoamperes (nA)/ppm or 0.27 nA/nanogram (ng) of tin. The noise level for the 1 nA range of the instrument was about 0.05 nA; this yields a value of 0.54 ng for the minimum detectable quantity of tin injected.

Results of all LCEC runs are summarized in Table 4. The most notable trends are the increase in sensitivity to tin with increasing methanol concentration and with increasing PCV concentration for a given mobile phase.

Attempts were made to form the Sn-PCV complex in situ by injection of standard Sn(IV) solutions into mobile phases containing PCV. Mobile phases containing more than 50 ppm PCV yielded background currents too high to permit onscale current readings, and only the 500 nA range of the instrument (the highest range available) could be employed. No signals ascribable to the Sn-PCV complex were observed.

SUMMARY

The investigations described in this report have yielded two novel electrochemical methods for detection and quantitation of inorganic Sn(IV). Although they do not offer enhanced sensitivity, these new methods offer advantages of convenience over known electrochemical methods. The voltammetric method has shown problems of reproducibility that need further study. The optimum concentration range for the voltammetric method appears to be 1.5×10^{-6} to 5×10^{-5} g-atoms/L (200 parts per billion (ppb) to 6 ppm) of tin. The best results for the LCEC method were obtained for tin concentrations of 2.5×10^{-5} to 1.7×10^{-4} gram-atoms/L (3 to 20 ppm). This does not approach the parts per trillion sensitivity needed for on-site monitoring of natural waters. Preconcentration would be necessary, as well as conversion of organotin to inorganic tin.

REFERENCES

1. M. L. Good, C. P. Monaghan, V. H. Kulkarni, and J. F. Hoffman. "Chemical and Physical Characterization of Organotin-Containing Marine Antifoulant Coatings," Org. Coat. Plast. Chem., Vol. 39 (1978), pp. 578-81.
2. C. P. Monaghan, E. J. O'Brien, Jr., H. Reust, and M. L. Good. "Current Status of the Chemical Speciation of Organotin Toxicants in Antifoulants," Dev. Ind. Microbiol., Vol. 21 (1980), pp. 211-15.
3. M. Whitfield and D. R. Turner. Marine Electrochemistry. M. Whitfield and D. Jagner, eds. New York, John Wiley and Sons, 1981, p. 54.
4. R. S. Braman and M. A. Tompkins. "Separation and Determination of Nanogram Amounts of Inorganic Tin and Methyltin Compounds in the Environment," Anal. Chem., Vol. 51 (1978), pp. 12-19.
5. Y. K. Chau, P. T. S. Wong, and G. A. Bengert. "Determination of Methyltin(IV) and Tin(IV) Species in Water by Gas Chromatography/Atomic Absorption Spectroscopy," Anal. Chem., Vol. 54 (1982), pp. 246-249.
6. V. F. Hodge, S. L. Seidel, and E. D. Goldberg. "Determination of Tin(IV) and Organotin Compounds in Natural Waters, Coastal Sediments and Macro Algae by Atomic Absorption Spectrometry," Anal. Chem., Vol. 51 (1979), pp. 1256-59.
7. B. Fleet and N. B. Fouzder. "Electrochemical Behaviour of Organotin Compounds. Part I. Application to the Determination of Trialkyl- and Triaryltin Derivatives," J. Electroanal. Chem., Vol. 63 (1975), pp. 59-68.
8. T. L. Shkorbatova, L. D. Sirak, G. G. Belous, F. A. Lutsenko, and D. A. Kochkin. "Polarographic Determination of Small Concentrations of Trialkyl-Substituted Organotin Compounds," Zh. Obshch. Khim., Vol. 48 (1978), pp. 1385-89.
9. M. D. Booth and B. Fleet. "Electrochemical Behavior of Triphenyltin Compounds and Their Determination at Submicrogram Levels by Anodic Stripping Voltammetry," Anal. Chem., Vol. 42 (1970), pp. 825-31.

10. H. B. Corbin. "Rapid and Sensitive Pyrocatechol Violet Method for Tin," Anal. Chem., Vol. 45 (1973), pp. 534-37.
11. M. Omar and H. J. M. Bower. "Preconcentration of Environmental Tin and Its Determination Using Catechol Violet," Analyst, Vol. 107 (1982), pp. 654-58.
12. W. D. Wakley and L. P. Varga. "Stability Constants of Tin-Pyrocatechol Violet Complexes From Computer Analysis of Absorption Spectra," Anal. Chem., Vol. 44 (1972), pp. 169-78.

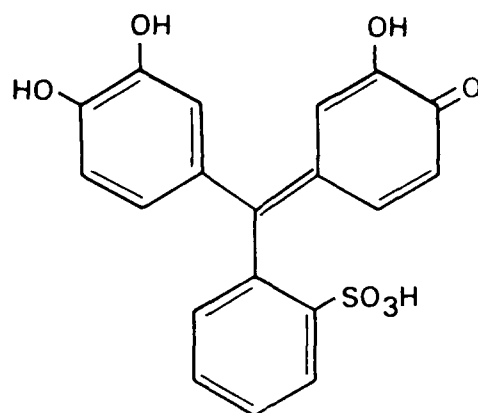


FIGURE 1. Structure of PCV.

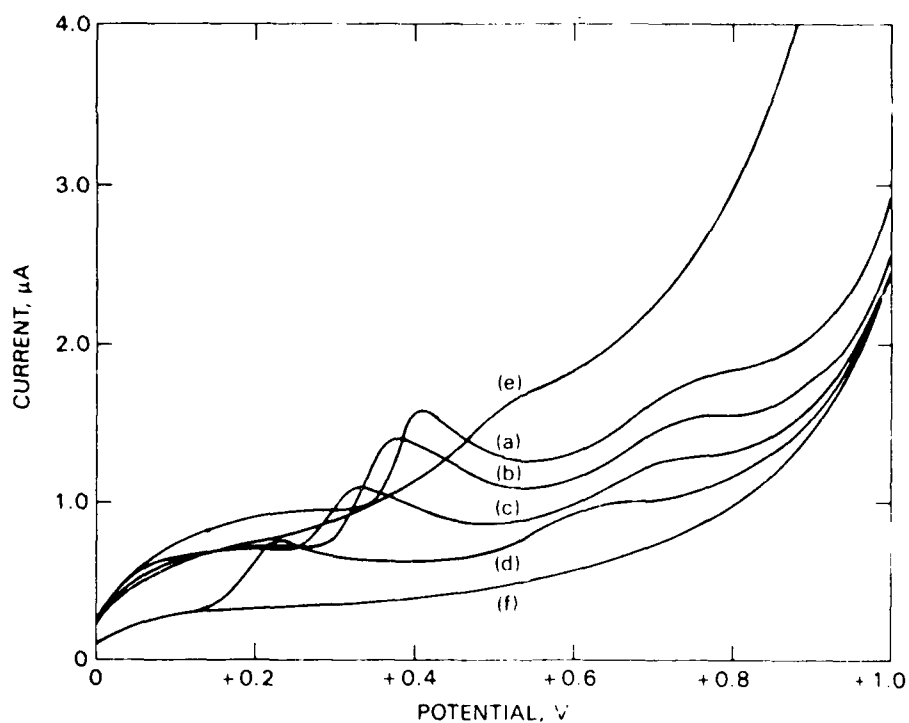


FIGURE 2. Linear Sweep Voltammograms of Solutions of 2.6×10^{-5} M PCV in 0.1 M NaCl, pH Adjusted With HCl, Ammonium Hydroxide (NH_4OH). Scan rate: 20 mV/s. pH: (a) 1.7; (b) 2.2; (c) 3.2; (d) 4.8; (e) 9.1; (f) blank solution (no PCV), pH 1.7.

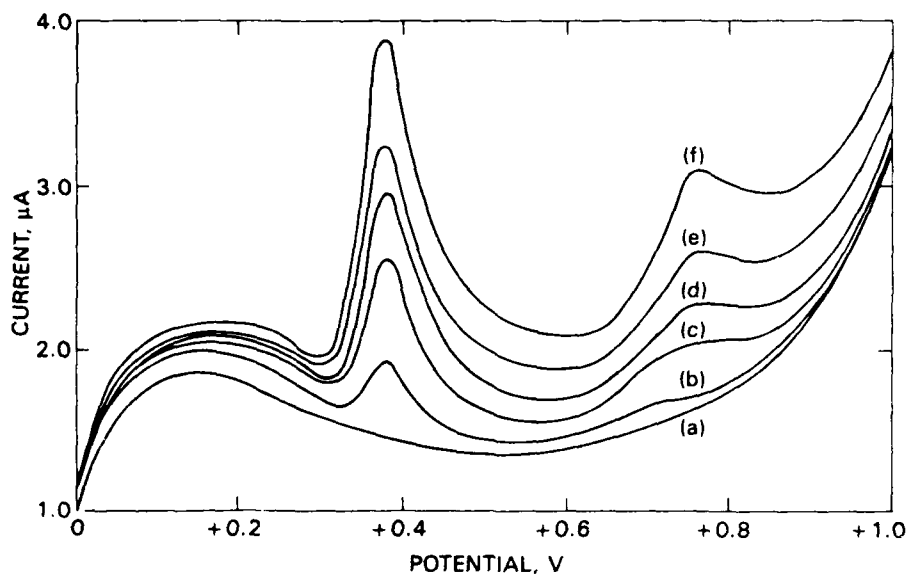


FIGURE 3. Linear Sweep Voltammograms of PCV in 0.1 M NaCl, pH = 2.2 (HCl). Scan rate: 20 mV/s. Concentration of PCV, M: (a) 0.0; (b) 8.4×10^{-6} ; (c) 3.4×10^{-5} ; (d) 5.0×10^{-5} ; (e) 5.9×10^{-5} ; (f) 1.0×10^{-4} .

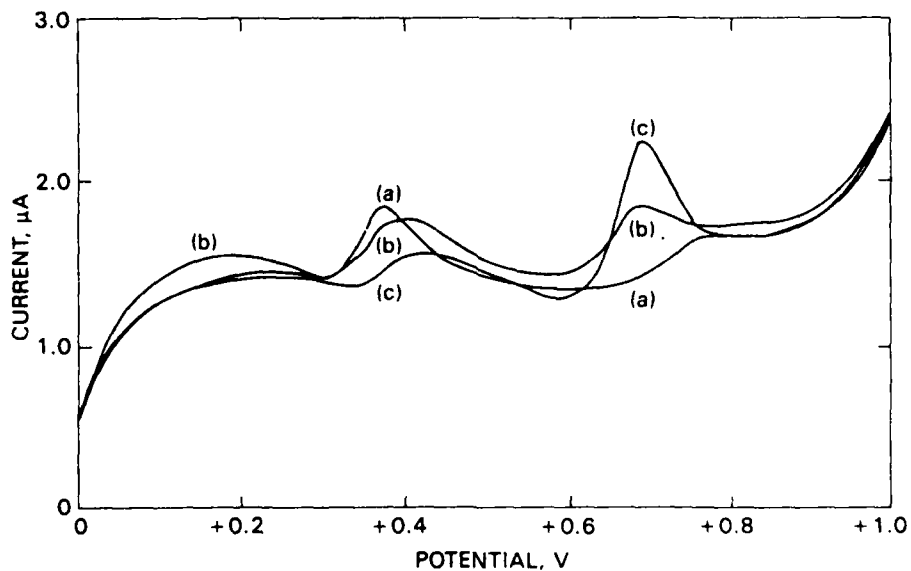


FIGURE 4. Linear Sweep Voltammograms of PCV Plus Sn(IV) in 0.1 M NaCl, pH = 2.0 (HCl). Scan rate: 20 mV/s. Concentration of PCV: 2.5×10^{-5} M. Concentration of Sn(IV), g-atoms/L: (a) 0.0; (b) 8.6×10^{-6} ; (c) 1.7×10^{-5} .

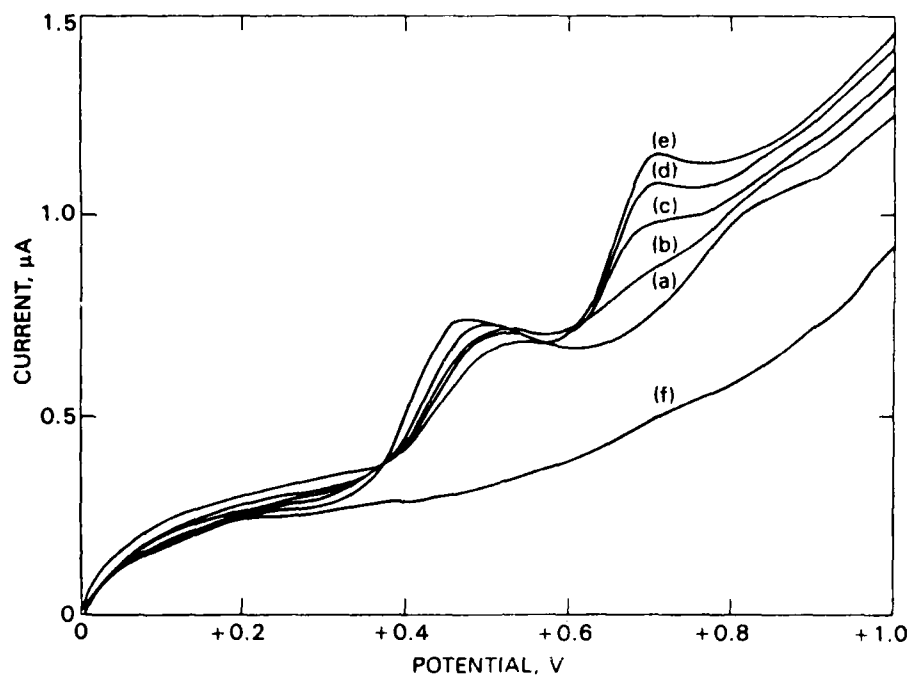


FIGURE 5. Linear Sweep Voltammograms of PCV Plus Sn(IV) in 30% MeOH, Buffered to pH 2.3 (HClOAc/NaOAc). Scan rate: 20 mV/s. Concentration of PCV: 5.2×10^{-5} M. Concentration of Sn(IV), g-atoms/L: (a) 0.0; (b) 3.2×10^{-6} (0.38 ppm); (c) 6.5×10^{-6} (0.77 ppm); (d) 9.6×10^{-6} (1.1 ppm); (e) 1.3×10^{-5} (1.5 ppm); (f) blank solution (no PCV).

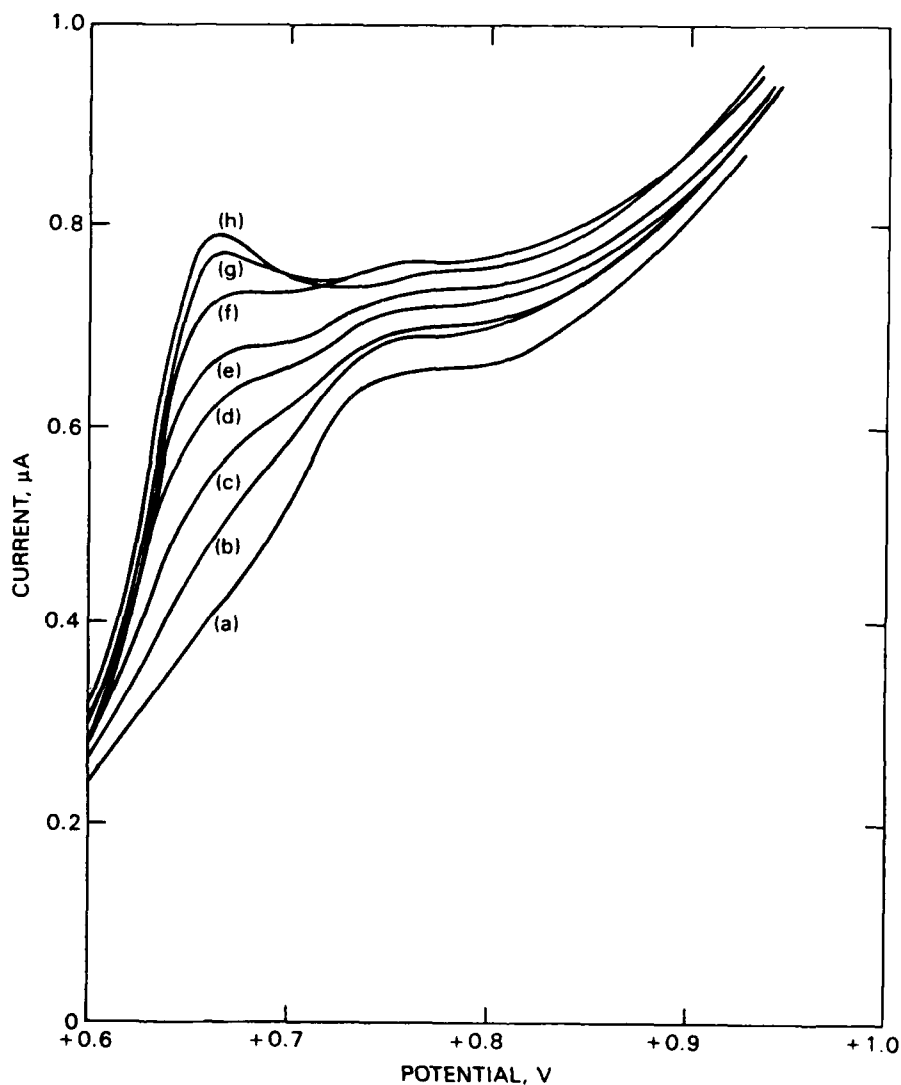


FIGURE 6. Linear Sweep Voltammograms of PCV Plus Sn(IV) in 30% MeOH, Buffered to pH 2.3 (HClOAc/NaOAc). Scan rate: 20 mV/s. Concentration of PCV: 5.2×10^{-5} M. Concentration of Sn(IV), g-atoms/L: (a) 0.0; (b) 1.6×10^{-6} (0.19 ppm); (c) 3.2×10^{-6} (0.38 ppm); (d) 4.8×10^{-6} (0.58 ppm); (e) 6.5×10^{-6} (0.77 ppm); (f) 8.1×10^{-6} (0.96 ppm); (g) 9.6×10^{-6} (1.1 ppm); (h) 1.3×10^{-5} (1.5 ppm).

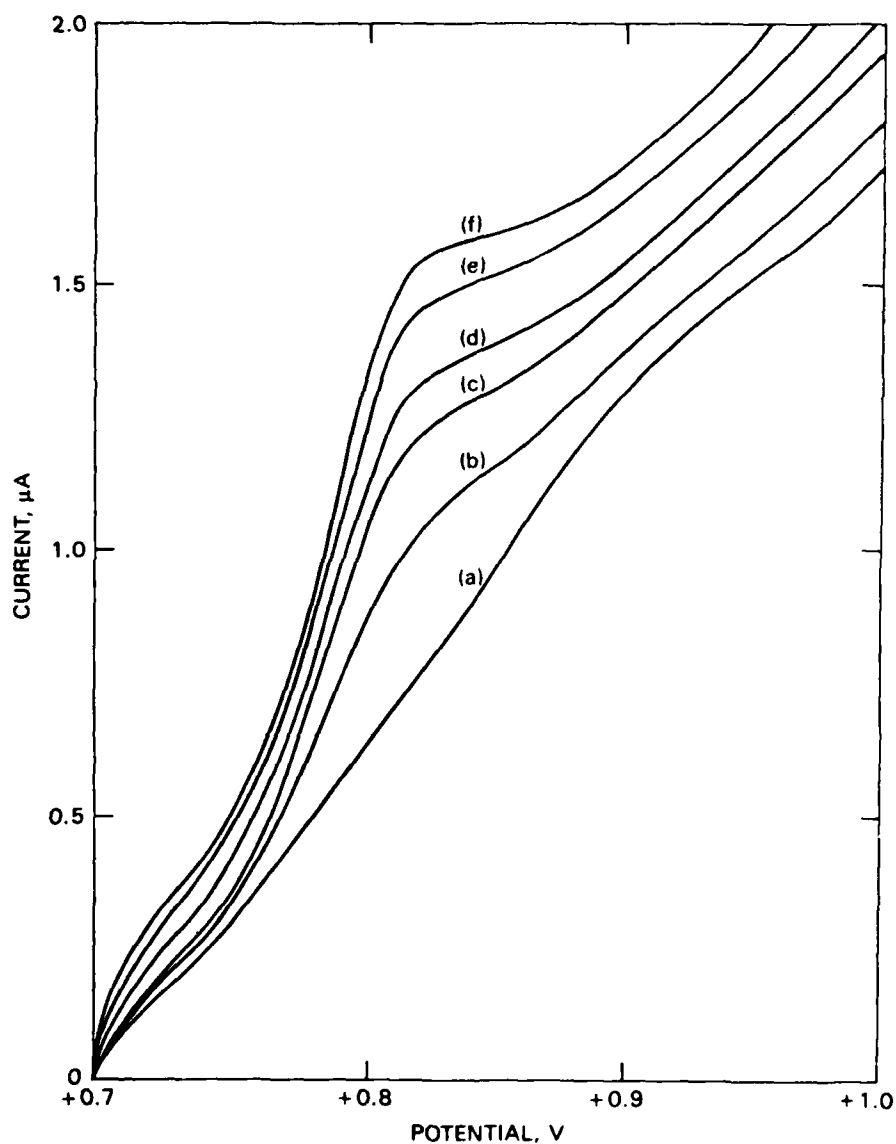


FIGURE 7. Linear Sweep Voltammograms of PCV Plus Sn(IV) in 30% MeOH, Buffered to pH 2.3 (HClOAc/NaOAc). Scan rate: 20 mV/s. Concentration of PCV: 2.6×10^{-4} M. Concentration of Sn(IV), g-atoms/L: (a) 0.0; (b) 4.2×10^{-6} (0.50 ppm); (c) 8.4×10^{-6} (1.0 ppm); (d) 1.3×10^{-5} (1.5 ppm); (e) 1.7×10^{-5} (2.0 ppm); (f) 2.1×10^{-5} (2.5 ppm).

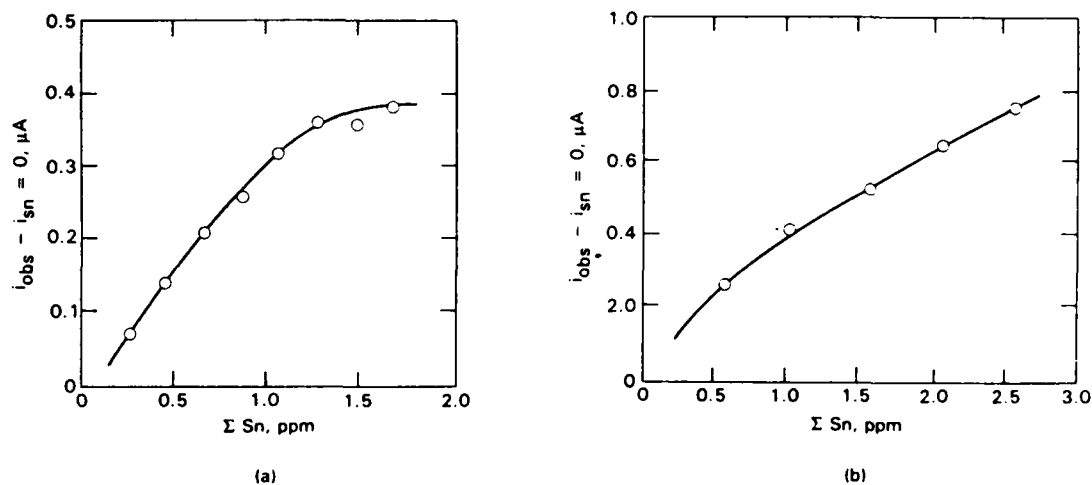


FIGURE 8. Plots of $i_{\text{obs}} - i_{\text{Sn}=0}$ versus ΣSn for (a) data from Figure 6 for $E = +0.650$ V and (b) data from Figure 7 for $E = +0.820$ V.

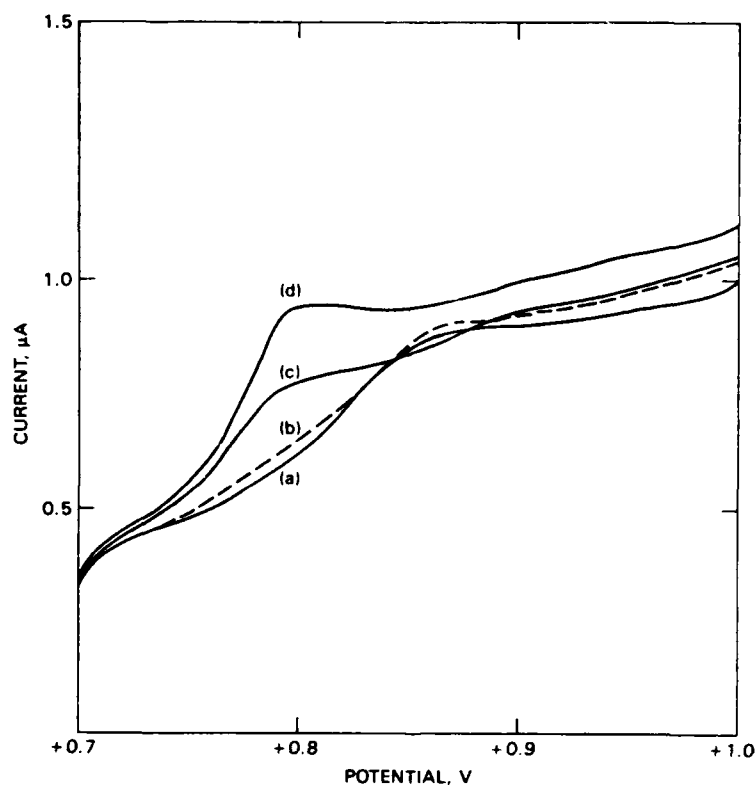


FIGURE 9. Linear Sweep Voltammograms With Conditions as in Figure 5. (a) PCV, 5.2×10^{-5} M; (b) Same PCV solution plus Bu_3SnCl (2.4 ppm); (c) Bu_3SnCl , after fuming with H_2SO_4 , dilution and addition to 5.2×10^{-5} M PCV (equivalent to 0.88 ppm tin); (d) same, with Bu_3SnCl equivalent to 1.76 ppm tin.

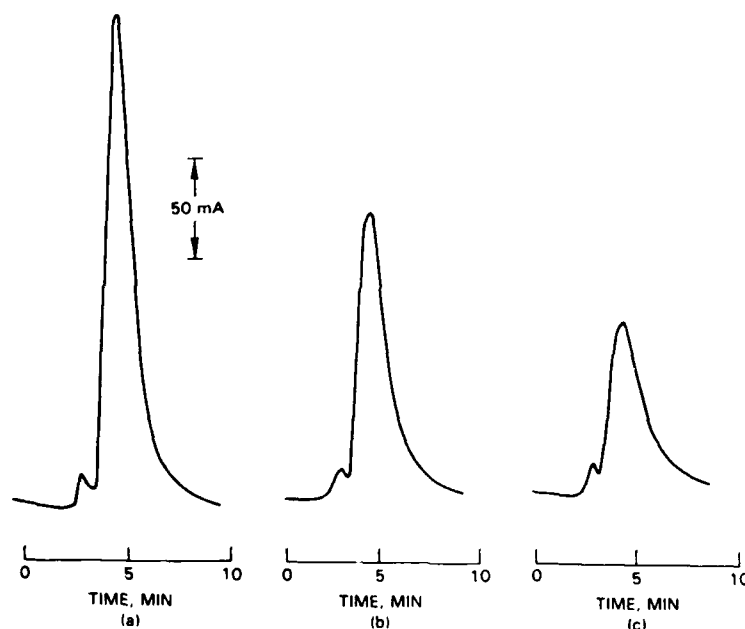


FIGURE 10. LCEC Chromatograms of Solutions Containing 200 ppm PCV, With Sn(IV) Concentrations of (a) 0 ppm; (b) 10 ppm; (c) 20 ppm. Mobile phase: 0.04 M HClOAc/0.01 M NaOAc in 50/50 v/v methanol/water. Flow rate: 1.0 mL/min. Injection volume: 20 L. Potential of GCE: +0.800 V (SCE).

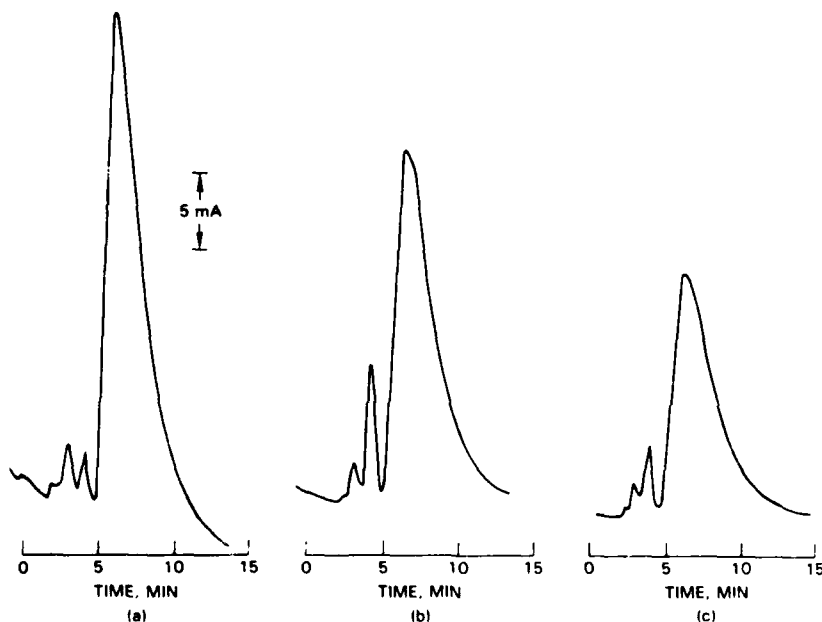


FIGURE 11. LCEC Chromatograms of Solutions Containing 50 ppm PCV, With Sn(IV) Concentrations of (a) 0 ppm; (b) 2 ppm; (c) 4 ppm. Mobile phase: 45/55 v/v methanol/water. Other conditions as in Figure 10.

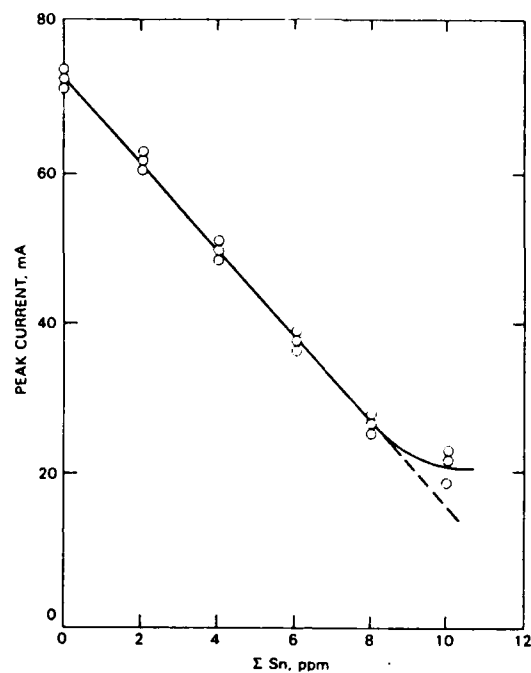


FIGURE 12. Peak Current vs Sn(IV) Concentration for Solutions Containing 100 ppm PCV. Results for 3 runs at each concentration are shown. Conditions as in Figure 11.

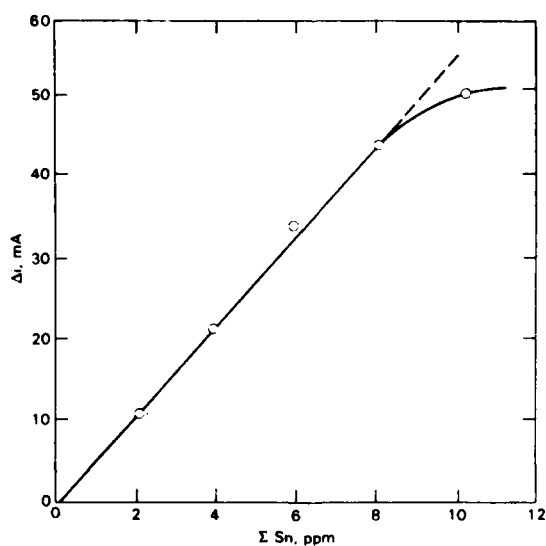


FIGURE 13. Decrease in Peak Current i versus Sn(IV) Concentration Using Average Values for Series Shown in Figure 12.

TABLE 1. Effect of pH on Voltammetric Properties of PCV.^a

pH	Color	E _p , ^b V	E _{wave} , ^c V
-0.5	Cherry red	+0.455	...
0.22	Orange-red	0.43	...
1.0	Orange	0.42	...
1.5	Yellow	0.395	+0.80
2.0	Yellow	0.37	0.80
3.0	Yellow	0.34	0.80
4.1	Yellow	0.295	0.75
4.8	Yellow	0.23	0.65
6.5	Dull yellow	0.18	0.60
7.8	Greenish purple	0.08	0.55
8.3	Purple-blue	0.1 ^d	0.55
8.7	Purple	...	0.55
9.1	Violet	...	0.55 ^e
10.0	Violet	...	0.52 ^f

^a Data from linear sweep voltammograms of solutions in 0.1 M NaCl, pH adjusted with HCl, NH₄OH. PCV concentration: 2.6×10^{-5} M. Scan rate: 20 mV/s.

^b E_p = potential at peak.

^c E_{wave} = potential of wave.

^d Plateau.

^e Shallow.

^f Very shallow.

TABLE 2. Effect of Addition of Sn(IV) on Linear Sweep Voltammograms of PCV.^a

pH	Effect of Sn(IV) addition	Potentials and values of maximum Δi [V: μA] ^b
0.22	Small maximum at +0.30, wave about +0.7	[+0.30:0.14], [+0.70:0.17]
1.0	Small maximum at +0.29, shift of maximum at +0.37 to +0.45, wave about +0.72	[+0.30:0.12], [+0.46:0.20], [+0.72:0.24]
1.5	Small maximum at +0.26, shift of maximum at +0.39 to +0.44, wave at +0.72. Color change from yellow to orange.	[+0.27:0.15], [+0.39:0.27], [+0.70:0.23]
2.0	Shift of maximum at +0.37 to +0.42, appearance of peak at +0.69. Color change from yellow to orange-red.	[+0.37:0.50], [+0.69:1.07]
3.0	Shift of maximum at +0.34 to +0.39, appearance of peak at +0.69. Color change from yellow to orange-red to purple.	[+0.34:0.51], [+0.69:1.05]
4.1	Small wave at +0.17, shrinkage of peak at +0.29, appearance of peak at +0.69. Color change from yellow to deep rose to purple.	[+0.29:0.46], [+0.69:1.12]

^a Concentration of PCV = 2.6×10^{-5} M; Concentration of Sn(IV): 8.6×10^{-6} M. Other conditions as in Table 1.

^b Δi = Change in current, V = potential, volts vs. SCE; μA = Δi , microamperes.

TABLE 3. Effect of Mobile Phase Solvent Composition on Retention Time and Height of Main Peak for Solutions Containing 200 ppm (5.2×10^{-4} M) PCV.

% MeOH	t_R , min	Average peak height, nA ^a
30	21.0	85
45	4.9	135
48	4.3	159
50	3.9	241

TABLE 4. Summary of Results of LCEC Runs for Solutions of PCV Plus Sn(IV).^a

% MeOH	ΣPCV, ppm	ΣSn, ppm	t _R , min	Peak height, nA ^b	ΔnA/ng Sn ^c
30	200.0	30.0	23.0	24.4	0.10
30	200.0	20.0	22.0	32.4	0.13
30	200.0	10.0	21.0	52.0	0.16
30	200.0	0.0	21.0	84.8	...
40	25.0	2.0	9.6	5.4	0.11
40	25.0	1.0	9.4	7.7	0.11
40	25.0	0.0	9.4	9.8	...
40	10.0	0.8	10.5	1.96	0.067
40	10.0	0.4	10.7	2.55	0.060
40	10.0	0.0	10.2	3.03	...
45	100.0	10.0	4.2	22.1	0.25
45	100.0	8.0	4.2	27.3	0.28
45	100.0	6.0	4.1	37.1	0.29
45	100.0	4.0	4.0	50.0	0.27
45	100.0	2.0	4.0	61.1	0.27
45	100.0	0.0	4.0	71.9	...
45	50.0	4.0	4.4	18.4	0.22
45	50.0	3.0	4.3	19.2	0.28
45	50.0	2.0	4.3	23.9	0.30
45	50.0	1.5	4.3	27.1	0.29
45	50.0	1.0	4.2	29.7	0.31
45	50.0	0.0	4.1	35.8	...
45	25.0	2.0	4.4	11.8	0.16
45	25.0	1.0	4.5	14.0	0.22
45	25.0	0.0	4.2	18.3	...
50	200.0	20.0	4.2	87.0	0.40
50	200.0	10.0	4.1	148.0	0.48
50	200.0	0.0	3.9	245.0	...
50	100.0	10.0	5.0	31.2	0.29
50	100.0	7.0	5.3	39.6	0.36
50	100.0	5.0	5.1	55.5	0.34
50	100.0	3.0	4.9	73.1	0.27
50	100.0	0.0	4.5	89.3	...

^a Mobile phases were methanol/water, buffered to pH 2.3 with HClOAc/NaOAc. Flow rate = 1.0 mL/min. Potential of GCE = +0.800 V versus SCE.

^b Average values for 2 to 5 runs.

^c ΔnA = decrease in peak height from run with no tin; average values for 2 to 5 runs.

INITIAL DISTRIBUTION

- 7 Naval Air Systems Command
 - AIR-5004 (2)
 - AIR-536A1 (1)
 - AIR-93D, G. Heiche (1)
 - AIR-931 (1)
 - AIR-933 (1)
 - AIR-935 (1)
- 5 Chief of Naval Operations
 - OP-225 (1)
 - OP-354 (1)
 - OP-506 (1)
 - OP-982E (1)
 - OP-982F (1)
- 3 Chief of Naval Research, Arlington
 - OCNR-440 (1)
 - OCNR-443 (1)
 - OCNR-470 (1)
- 3 Naval Facilities Engineering Command, Alexandria
 - Code 032, S. Hurley (1)
 - Code 112 (1)
 - Code 54 (1)
- 7 Naval Sea Systems Command
 - SEA-04E (1)
 - SEA-05R1 (1)
 - SEA-05R14 (1)
 - SEA-05R16 (1)
 - SEA-09B312 (2)
 - SEA-62D4 (1)
- 1 Commander in Chief, U.S. Pacific Fleet, Pearl Harbor (Code 325)
- 1 Marine Corps Development and Education Command, Quantico (Marine Corps Landing Force Development Center)
- 1 Commander, Third Fleet, Pearl Harbor
- 1 Commander, Seventh Fleet, San Francisco
- 1 David W. Taylor Naval Ship Research and Development Center, Bethesda (Code 2862, P. Schatzberg)
- 2 Naval Academy, Annapolis (Director of Research)
- 2 Naval Air Development Center, Warminster
 - Code 606 (1)
 - Library (1)
- 1 Naval Air Propulsion Center, Trenton (PE-71, A. F. Klarman)
- 7 Naval Civil Engineering Laboratory, Port Hueneme
 - LO3AP, E. Early (1)
 - L52, E. Lory (1)
 - L54
 - D. Chan (1)
 - J. Crane (1)
 - C. Imel (2)
 - L59, D. Brunner (1)
- 1 Naval Coastal Systems Center, Panama City (Code 112.2)
- 1 Naval Energy and Environmental Support Activity, Port Hueneme

- 2 Naval Explosive Ordnance Disposal Technology Center, Indian Head
 - Code RD (1)
 - Technical Library (1)
- 1 Naval Intelligence Support Center (NISC-80, Library)
- 3 Naval Ocean Systems Center, San Diego
 - Code 513
 - S. Yamamoto (1)
 - A. Zirmo (1)
 - Code 5131, M. H. Salazar (1)
- 2 Naval Ordnance Station, Indian Head
 - Code E, Pollution Abatement Program Manager (1)
 - Technical Library (1)
- 3 Naval Research Laboratory
 - Code 4300 (1)
 - Code 6100 (1)
 - Library (1)
- 5 Naval Surface Weapons Center, Dahlgren
 - G-51
 - J. Bromfield (1)
 - D. Knudsen (1)
 - R. Gibbs (1)
 - Code 651, D. Rowe (1)
 - Technical Library (1)
- 5 Naval Surface Weapons Center, White Oak Laboratory, Silver Spring
 - Code R11 (2)
 - Code R16, J. Hoffsommer (1)
 - Code R17 (1)
 - Code R141, G. Young (1)
- 1 Naval Underwater Systems Center, Newport (Code 364, R. Kronk)
- 1 Naval War College, Newport
- 1 Naval Weapons Station, Concord (Code 321, M. Bucher)
- 2 Naval Weapons Station, Yorktown
 - Code 203, M. West (1)
 - Code 50 (1)
- 4 Naval Weapons Support Center, Crane
 - Code 3025, D. Burch (1)
 - Code 50C, B. E. Douda (1)
 - Code 505, L. Craig (1)
 - Code 90, A. E. Whitner (1)
- 1 Pacific Missile Test Center, Point Mugu (Code 2145)
- 1 Theatre of Nuclear Warfare Project Office (TN-20A, G. Patton)
- 1 Army Armament Munitions and Chemical Command, Rock Island
- 13 Army Armament Research, Development and Engineering Center, Picatinny Arsenal, Dover
 - DRDAR-LCA (2)
 - DRDAR-LCE (2)
 - DRDAR-LCE-C, Chemistry Branch (1)
 - DRDAR-LCE-D (2)
 - DRDAR-LCM (2)
 - DRDAR-LCM-SA, R. Westerdahl (1)
 - DRDAR-LCU (2)
 - SMCAR-FSM-E (1)
- 4 Army Ballistic Research Laboratory, Aberdeen Proving Ground
 - DRDAR-BLP, Watermeier (1)
 - DRDAR-BLT, P. Howe (2)
 - DRDAR-TSB-S (STINFO) (1)
- 1 Army Environmental Hygiene Agency, Aberdeen Proving Ground (HSHB-EA-A)
- 1 Army Medical Bioengineering Research and Development Laboratory, Fort Dietrick (J. Barkeley)
- 1 Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground (DRXTH-TE-D)
- 1 Radford Army Ammunition Plant (SARRA-EN)
- 1 Tooele Army Depot, Chemical Systems Engineering (J. Bishop)

3 Air Force Systems Command, Andrews Air Force Base

DLFP (1)

DLWA (1)

SDZ (1)

4 Air Force Armament Division, Eglin Air Force Base

AFATL/DLDE (1)

AFATL/DLJW (1)

AFATL/DLODL (1)

D. Harrison (1)

12 Defense Technical Information Center, Alexandria

1 Battelle Memorial Laboratory, Tactical Technical Information Center, Columbus, OH

1 Holston Defense Corporation, Kingsport, TN (Plant Manager)

3 Johns Hopkins University, Applied Physics Laboratory, Chemical Propulsion Information Agency, Laurel, MD

T. W. Christian (2)

J. Hannum (1)

1 Los Alamos National Laboratory, Los Alamos, NM (H. Flaugh)

2 University of California, Lawrence Livermore National Laboratory, Livermore, CA

Organic Materials Division

R. R. McGuire (1)

D. L. Ornellas (1)